15

ADSORPTION AND CATALYSIS

ADSORPTION

- The phenomenon of attracting and retaining the molecules of a gas or a dissolved substance by the surface of a solid, resulting in their higher concentration on the surface is called ***adsorption***.
- The substance which gets adsorbed is called the ***adsorbate*** and the solid substance which adsorbs is called the ***adsorbent***.

Adsorption and Absorption

- **Absorption:** It is the process in which a fluid is dissolved by a liquid or a solid (absorbent).
- **Adsorption**: It is the process in which atoms, ions or molecules from a substance (it could be gas, liquid or dissolved solid) adhere to a surface of the adsorbent**.**

Factors Affecting Adsorption

- Adsorption occurs on the surface of almost all solids. However, the extent of adsorption of a gas on the surface of a solid depends upon the following factors:

(i) Nature and surface area of the adsorbent
(ii) Nature of the adsorbed gas
(iii) Temperature
(iv) Pressure of the gas

Physical and Chemical Adsorption

- In ***physical adsorption***, adsorbate is held to adsorbent by weak *van der Waals* forces. In ***chemisorptions***, adsorbate is held to adsorbent by strong chemical bond type of forces.

Adsorption Isotherms

- The extent of adsorption is measured in terms of the quantity x m where, x is the mass of the gas (adsorbate) adsorbed at equilibrium on mass m of the adsorbent. x m is the mass of the adsorbate adsorbed per unit mass of the adsorbent. The graph showing variation in x m with pressure (p) at a constant temperature is called ***adsorption isotherm.***
- **The variation in extent of adsorption in case of gases and of solutes from their solutions.**

(i) Adsorption of Gases

- The adsorption isotherm of a gas shows that the extent of adsorption of a gas on a solid increases with the increase in the pressure of the gas, p at three different constant temperatures.

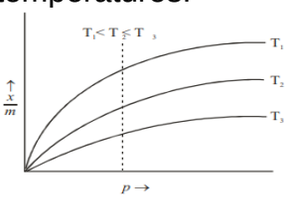

Fig. 15.1: Adsorption isotherm of a gas

- **Freundlich Adsorption Isotherm:** Freundlich gave an empirical mathematical relationship between the extent of adsorption (x/m) and the equilibrium pressure (p) of the gas as :

$$\frac{x}{m} = k\, p^{\frac{1}{n}} \quad \text{where } n > 1 \qquad \textit{i.e.,} \qquad \log \frac{x}{m} = \log k + \frac{1}{n} \log p$$

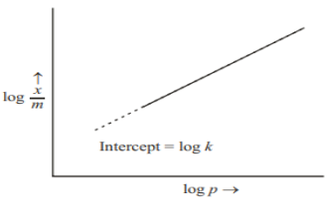

Fig. 15.2: Plot of log x /m against log p

This is an equation of a straight line and a plot of log x/m against log p should be a straight line with slope 1/n as depicted in ***Fig. 15.2.***

Langmuir Adsorption Isotherm

- The Langmuir adsorption isotherm is used to describe the equilibrium between adsorbate and adsorbent system, where the adsorbate adsorption is limited to one molecular layer at or before a relative pressure of unity is reached**.**

$$\frac{m}{x} = \frac{1 + bp}{ap} = \frac{b}{a} + \frac{1}{ap}$$

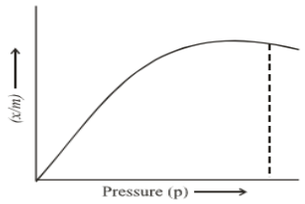

Fig. 15.3: Langmuir Adsorption isotherm.

A plot of m/x against 1/p gives a straight line the slope and intercept equal to 1/a and b/a, respectively. Thus, both parameters can be determined.

(ii) Adsorption from Solutions: Adsorption occurs from solutions also. The solute gets adsorbed on the surface of a solid adsorbent. Charcoal, a good adsorbent, is often used to adsorb acetic acid, oxalic acid and organic dyestuffs from their aqueous solutions.

CATALYSIS

- The phenomenon of change of reaction rate by addition of a substance which itself remains unchanged chemically is called ***catalysis***. For Example: The evolution of hydrogen by the reaction between zinc and hydrochloric acid is catalysed by Cu^{2+}(aq) ions.

$$Zn(s) + 2HCl(aq) \xrightarrow{Cu^{2+}(aq)} ZnCl_2(aq) + H_2(g)$$

- **Catalyst:** A catalyst is a substance which changes the rate of a reaction but remains chemically unchanged at the end of the reaction.
- **Auto-catalysis:** In autocatalysis, the reaction is catalyzed by one of its products and that catalyst is called ***Autocatalyst***. One of the simplest examples of this is in the oxidation of a solution of oxalic acid by an acidified
- **Negative Catalysis:** Some catalysts retard a reaction rather than speed it up. They are known as negative catalysts. ***For example*:**

(i) Glycerol retards the decomposition of hydrogen peroxide.

(ii) Phenol retards the oxidation of sulphurous acid.

- **Promoters and Poisons:** The substances which increase the activity of a catalyst are called promoters and those which decrease the activity of a catalyst are called poisons. ***For example*:** In **Haber's process** for the manufacture of ammonia, the catalytic activity of iron is enhanced by **molybdenum** which acts as promoter.

General Characteristics of a Catalyst

(i) A catalyst remains unchanged at the end of the reaction.

(ii) A small quantity of the catalyst is generally enough.

(iii) A catalyst does not alter the position of equilibrium state of a reversible reaction

(iv) Catalysts are generally specific in their action

(v) A catalyst cannot initiate a reaction.

Homogeneous and Heterogeneous Catalysis

- In ***homogeneous catalysis***, the catalyst is in the same phase as that of reactants and in ***heterogeneous catalysis***, the catalyst is in the different phase from the reactants.

Catalysis and Activation Energy

- A **catalyst** increases the rate of reaction without being consumed in the reaction. In addition, the **catalyst** lowers the **activation energy**, but it does not change the **energies** of the original reactants or products, and so does not change equilibrium.

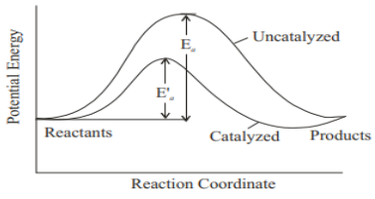

Fig. **15.4: Graphical representation of the effect of catalyst on a reaction.**

Check Yourself

1. In Freundlich adsorption isotherm x/m = Kp1/n, the value of 'n' at low pressure is

(A) More than one. (B) Less than one.

(C) Equal to one. (D) From zero to one.

2. Which shape selective catalyst is used to convert alcohol to gasoline?

(A) Tripsin (B) Calgon

(C) ZSM-5 (D) Zeigler-Natta catalysts

3. Which one of the following is an example of adsorption?

(A) Ammonia in contact with water
(B) Anhydrous $CaCl_2$ with water

(C) Silica gel in contact with water vapours

(D) all of these

4. At 15°C out of H_2, CH_4, CO_2, NH_3, which gas will be adsorbed maximum by charcoal?

(A) H_2 (B) CH_4

(C) CO_2 (D) NH_3

5. Homogeneous catalysis does mean

(A) Reactants and goods have to be at the same level

(B) Catalyst and reactants must be in the same phase

(C)The reaction mixture must be formed homogeneously during

(D) The reaction mixture distribution must be homogeneous

Stretch Yourself

1. "Chemisorption is highly specific" Illustrate with an example.

2. Mention one shape selective catalyst used to convert alcohol directly into gasoline.

3. Name the catalyst used in the following process:

(a) Haber's process for the manufacture of NH_3 gas.

(b) Ostwald process for the manufacture of nitric acid.

4. Write the difference between:

(a) Catalysts and enzymes

(b) Promoters and poisons

5. Mention two important features of solid catalysts and explain them with the help of suitable examples.

Test Yourself

Question: State the sign of entropy change involved when the molecules of a substance get adsorbed on a solid surface.

Answer: when the molecules get adsorbed on a solid surface their RANDOMNESS decreases. This implies there will NEGATIVE entropy change. i.e., entropy decreases.

Answers

Check Yourself

Answer: 1(C); 2(C); 3(C); 4(D); 5(B)

Stretch Yourself

1. Do it by yourself.

2. ZSM-5 is the shape selective catalyst used to convert alcohol directly into gasoline.

3. Hint:

(a) Finely divided Fe/FeO, MO as a promoter.

(b) Pt (platinised asbestos)

4. Do it by yourself.

5. Heterogeneous catalyst involves the use of a catalyst in a different phase from the reactants. Typical examples involve a solid catalyst with the reactants as either liquids or gases. In heterogeneous catalyst the reactants are adsorbed on the to the surface of the catalyst at active sites. There is interaction between the surface of the catalyst and the reactant molecules are finally desorbed.